

THE SALT RECOVERY PROCESS

Common salt (NaCl) is essential for human life. Much of New Zealand's salt needs are provided for from salt purified from the sea at Lake Grassmere, some of which is further refined at Mt. Maunganui. This salt has many uses in industry and agriculture, as well as being used for water softening, in the production of pharmaceuticals and other chemicals, and of course in food.

In New Zealand salt is initially purified by the solar process, and then is sometimes further purified by the vacuum process for applications where a high purity is required.

The solar salt process

Here sea water is pumped into Lake Grassmere, and pumped from there through a series of concentration ponds in which the water gradually evaporates out and some impurities are deposited. The saturated brine is then passed through a series of crystallisation ponds in which the salt gradually crystallises out, and finally the remaining brine is removed. This salt is harvested and washed with saturated clean brine to remove impurities, after which it is stacked for storage before being further purified or processed into a commercial product.

The production of vacuum salt

The solar salt still contains various impurities, which the vacuum process removes. The salt is dissolved in pure water and treated to remove impurities, after which the water is evaporated off by passing the solution through three chambers at progressively lower pressures. This forms a super-saturated solution from which salt precipitates, forming a slurry that is dried by centrifuging and fluid bed drying. This salt has a variety of uses in the food and pharmaceutical industries.

As this process has sea-water and pure water as its raw materials, all its by-products are harmless to the environment and can be discharged back into the sea.

INTRODUCTION

Sodium chloride, common salt, is essential to human life. Our bodies contain up to 450 grams of salt and we need to take in a few grams each week to stay healthy. The value of salt can be seen in the way Roman soldiers used to be paid in salt, leading to the phrase "worth his salt" and our word "salary". The growth of industry has increased the demand for salt, both for direct use and as a raw material for producing other chemicals.

Throughout the world the main sources of salt are sea water, lake water and rock salt deposits. Salt is recovered from the sea and lakes by evaporation. Rock salt may be mined like coal, or recovered by drilling wells into the salt bed, forcing down pure water, and pumping up the saturated brine which forms.

Two and a half percent by weight of seawater is salt (both sodium chloride and others). The early settlers in New Zealand tried to extract salt from the sea as early as the 1880's, but the first salt works were not opened until 1949. These were located at Lake Grassmere, Marlborough, and are still owned by the original operator, Dominion Salt Ltd. Here the

seawater is evaporated off using solar energy. The average annual output of salt from Lake Grassmere has risen from the 50.8 tonnes produced in 1949 to about 65 000 tonnes (record yield to date 116 500 tonnes in 1973), but this is still not enough to meet New Zealand's annual needs (125 000 tonnes in 1990, estimated to rise to 140 000 tonnes by the year 2000).

Thus New Zealand has always had to import salt. Although Grassmere's solar salt is of sufficient purity for many purposes, there is a large demand for a more refined product (vacuum salt). Prior to 1976 vacuum salt was imported, but in that year two refining plants were opened, one at Grassmere and the other at Mt. Maunganui, which process imported crude salt. The Mt. Maunganui site was chosen because it has first class port and rail facilities and close proximity to paper mills and other major processors.

Uses of salt

Although table salt is the most familiar form of common salt, it is responsible for only a small proportion of Dominion Salt's output. The largest user of salt in New Zealand is the meat industry, which uses salt in the treatment of hides and skins (see leather tanning article), although there are many other uses listed below.

Industrial applications

Metal recovery
Paper manufacture
Rubber processing
Road de-icing
Dyes & textiles
Ceramic glazing
Refrigerant brines
Water pollution control
Water Softeners

In Agriculture

Hide & skin
Stockfeed
Fertilizer
Farm drenching
Water troughs

Medical, cleansing

Chlor-alkali
Soap & cleaners
Dental, medical
Bath salts

Dairy products

Cheese salting
Butter making

Aquaculture

Fish brines
Fish processing
'Dry' salt fish processing
Fish canning
Chill fish (Fish slaughter)

Food preparation

Snackfoods
Breakfast Cereal
Bread
Cakes, biscuits
Confectionery
Industrial flavour
Catering
Casings
Margarine, fats
Cans & preserves
Brine making
Dry seasonings
Frozen foods

A variety of chemicals are also produced from sodium chloride, including:

Sodium carbonate
Chloroform
Sodium silicate
Trichlorobenzene
Calcium chloride

Hydrochloric acid
Caustic soda (NaOH)
Ethylene
Calcium chlorate
Sodium bicarbonate

Carbon tetrachloride
Sodium metabisulphite
Chlorine
Sodium hypochlorite
(bleach)

THE PURIFICATION PROCESS

Sea water is 2.5% salt by weight, one litre of sea water containing about 25 grams of salt. But sodium chloride is not the only salt present, there being appreciable amounts of calcium, magnesium and potassium cations, and sulphate and bromide anions, amongst others (**Table 1**). These are not wanted in the recovered salt. However, of these, only calcium sulphate is less soluble than sodium chloride, and the recovery process relies on this. The seawater is concentrated to the point at which calcium sulphate deposits, and then transferred to crystallising ponds where it is further concentrated, depositing sodium chloride, with the concentrating process stopped before the brine is sufficiently concentrated for other salts to crystallise out. A summary of the entire process carried out by Dominion Salt is given in **Figure 1**.

Table 1 - Concentrations of some ions found in seawater

Ion	Concentration		Ion	Concentration	
	mg L ⁻¹	mol L ⁻¹		mg L ⁻¹	mol L ⁻¹
Cl ⁻	19 000	0.536	Na ⁺	11 050	0.480
SO ₄ ²⁻	2652	2.760 x 10 ⁻²	Mg ²⁺	1 350	0.055
Br ⁻	65	8.134 x 10 ⁻⁴	Ca ²⁺	422	0.011
			K ⁺	416	0.011

Table 2 - Division of space at Lake Grassmere

Area	Number	Size / hectares	Use
Main lake (not stopbanked)	1	688	evaporation of half the water of incoming seawater
Concentrating ponds	15	567	step-by-step brine concentration to saturation strength
Deep storage ponds	4	20	winter storage of strong brines at depths of 3 to 5 metres
Crystallizing ponds	22	93	salt depositing
Re-concentrating ponds	5	40	concentrating rain-diluted brine
Wash brine ponds	4	8	washing salt during harvesting and rewashing stockpiled salt

The production of solar salt at Lake Grassmere

Sea water is pumped from the ocean through an intake to large ponds where energy in the form of sunshine and wind goes to work and evaporation begins. **Figure 2** shows the layout of the Lake Grassmere complex which covers 1800 hectares (4500 acres), used as shown in

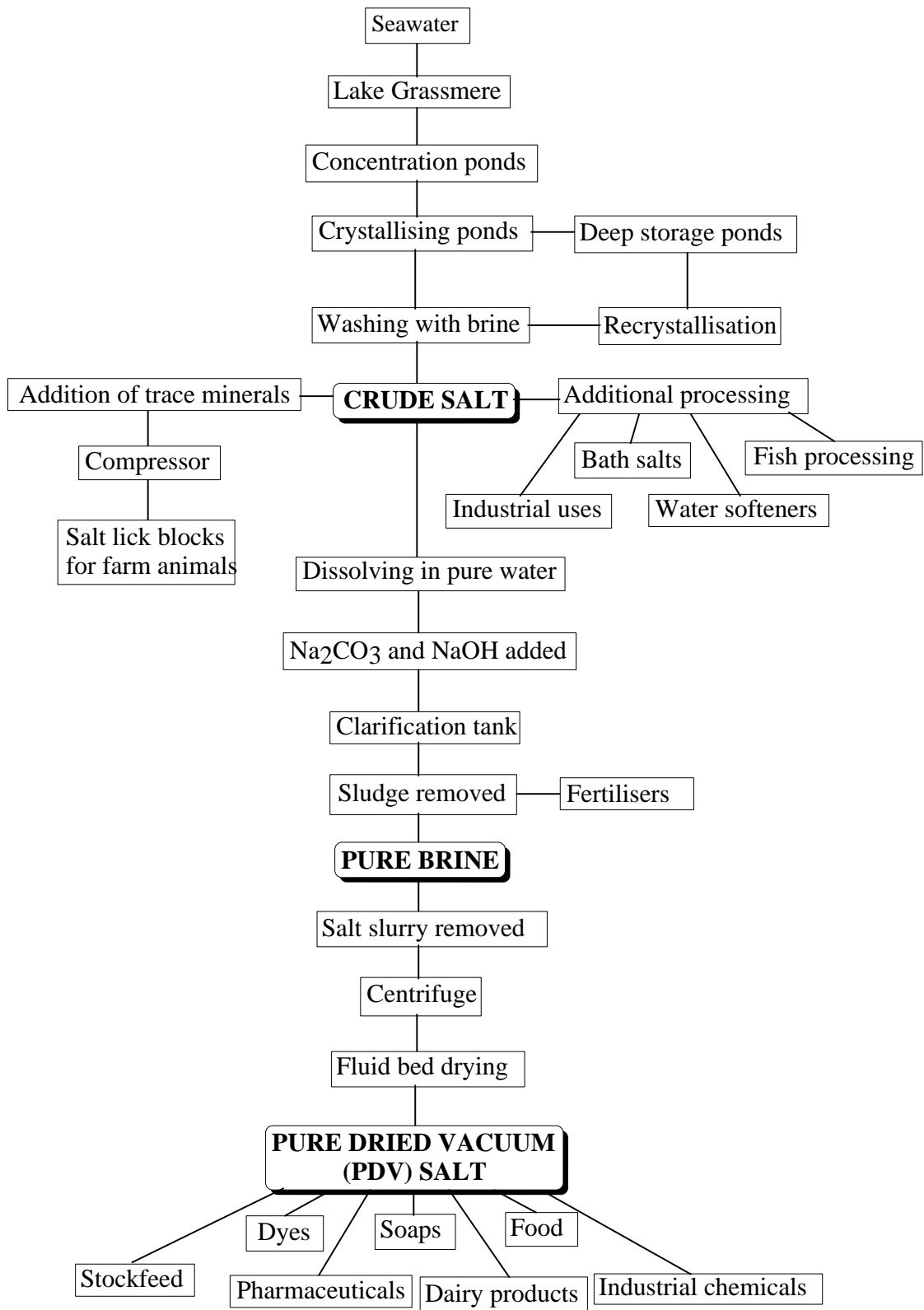


Figure 1 – Schematic representation of the salt recovery process

Table 2. As the evaporation requires a lot of solar energy, salt recovery is carried out only during the salt making 'season' (early October to early March), during which time salt water is pumped continuously into the main lake at rates of up to 40 tonnes per minute. During this time an average of 510 mm of water is evaporated off the surface of the brine

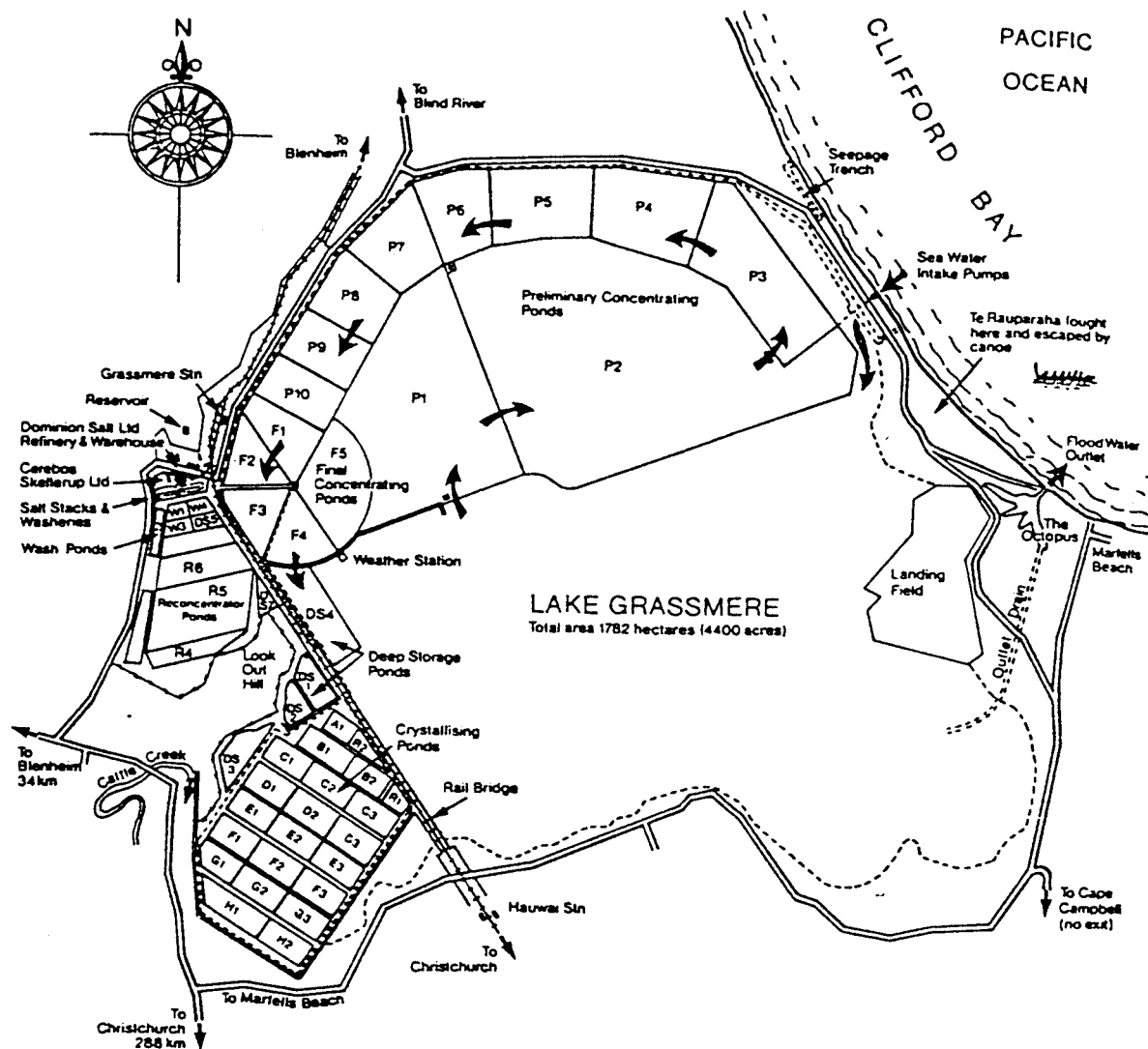


Figure 2 - The layout of the Lake Grassmere complex

The water volume is reduced in large ponds to 27.4% of the original, causing calcium sulfate to precipitate out. Note that an ionic species A_xB_y crystallises out of a solution when $[A]^x[B]^y > K_s^1$. It can be calculated from **Table 1** that in seawater

$$[Ca^{2+}][SO_4^{2-}] = 3.036 \times 10^{-4}$$

and when the volume is reduced to 27.4% of the original:

$$\begin{aligned} [Ca^{2+}][SO_4^{2-}] &= 0.04014 \times 0.1007 \\ &= 4.043 \times 10^{-3} \end{aligned}$$

The calcium sulfate crystallises out at this point, which would suggest that

$$K_s (CaSO_4) \approx 4.043 \times 10^{-3}.$$

However, in a table of K_s values, the value given for $CaSO_4$ is 2.4×10^{-5} - suggesting that even raw seawater is a supersaturated solution of calcium sulfate. This is because in solutions with high concentrations of ions the K_s values increase, due to interactions between ions which lower the affinity of cations for anions. Thus for calcium sulfate, K_s in freshwater is 2.4×10^{-5} , and in seawater it is 1.4×10^{-3} .

¹Note that K_s is the solubility product, i.e. the equilibrium constant of the dissolution of a salt in water.

The brine then passes on through the various ponds, with the sodium chloride content rising from 2% to 25%. This increasing salinity gives the ponds a distinctive pink colour, as algae in strongly saline solutions produce a red pigment called haematochrome. The Red Sea is red for the same reason.

The saturated brine is pumped to smaller ponds where nature continues its work of evaporation. Once the volume has been reduced to 10.2% of the original, $[Na^+][Cl^-] = 24.729$, and as $K_s(NaCl) = 24.730$, any further concentration results in the deposition of sodium chloride. From September to February more brine is added until at least 25 mm of salt has settled and it is time for harvesting. The brine remaining (called "bitterns") is a saturated solution of NaCl, with the other salts present at concentrations well below saturation. This is pumped out to sea just before the harvest is gathered, as these ions would contaminate the salt if all the water were evaporated off.

For four to six weeks beginning in early March, mechanical harvesters scoop up the crystallised salt and load it on to trucks that shuttle back and forth across the ponds to the washery. In the two washing plants the salt is washed in clean saturated brine, in which the other salts, present as impurities, dissolve. From there hundreds of tonnes of clean washed salt are discharged daily on to the stacks for storage - up to 6000 tonnes per day.

During winter no more salt is recovered, but the plant continues its regular work of processing and bagging the stockpiled salt.

There is very little room for expansion at Lake Grassmere and thus more solar salt than can be produced at Grassmere is required by New Zealand, both for current needs and for the establishment of chemical industries. The extra salt needed is imported as crude salt and processed by Dominion Salt.

The production of vacuum salt

Vacuum salt is a high purity, fine cubic-crystal salt formed by the artificial evaporation of chemically treated brine. It is evaporated under near-vacuum conditions to obtain maximum heating economy.

The Mt. Maunganui refinery operates on a round-the-clock basis, is almost entirely automatic, and is capable of producing over 5 tonnes an hour of pure dry salt. The plant even generates its own electricity and at times excess power can be fed into the local supply.

Figure 3 illustrates the main features of the plant.

The first step in this process is to dissolve crude salt to produce brine. Some of this brine is produced by the action of rain on the stockpiled solar salt, and by dissolving salt dust collected from industrial salt processing. Thus the rainfall at Mt. Maunganui - over 1270 mm (50 inches) a year - which would normally be regarded as a disadvantage to salt-making, is put to good use. Additional brine is made by sprinkling condensate from the evaporators back onto the bulk stockpile.

The brine has to be treated to remove residual chemicals and impurities deposited in the salt before recrystallisation. To achieve this, soda ash (Na_2CO_3) and caustic soda (NaOH) are mixed into the brine stream, causing calcium salts to precipitate as calcium carbonate and

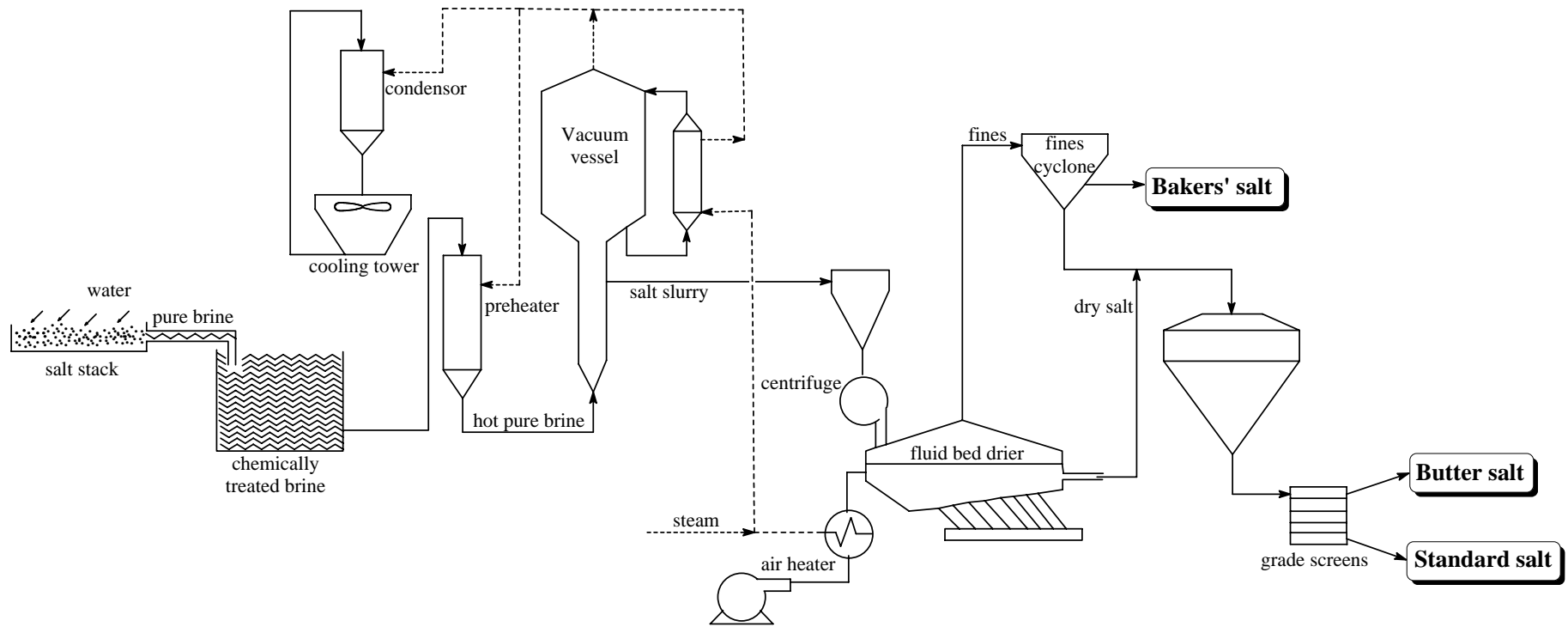


Figure 3 – The vacuum salt process

magnesium salts as magnesium hydroxide, while the sulphates are converted to highly soluble sodium sulphate. The treated brine is then clarified in a tank from which the precipitates are periodically removed as sludge and pumped to storage tanks. The sludge contains a calcium-magnesium compound with some salt and can be used as an additive to fertilisers. This treatment also has the useful side-effect of removing calcium compounds that would otherwise form scale and impede production.

The resultant pure brine is evaporated in a triple-effect plant. The first effect operates at close to atmospheric pressure and the third at near-vacuum, so the boiling point of the solution is lowered as it passes through the plant. The brine in each evaporator is drawn off through a loop and passed through a steam-heated heat exchanger, which causes the vapour from the brine to evaporate and salt crystals to form in the supersaturated solution. By circulating the boiling brine, minute seed crystals are carried in suspension until they grow to a size and weight that makes them fall to the stationary section of the conical base.

Vapour exhausted from the first effect is carried over to the second effect heat exchanger and in turn from the second to the third effect heat exchanger, thus giving the most economical heating. Vapour from the third effect passes to a direct contact condenser and is extracted in the cooling tower water circuit. Condensate from the heat exchangers is fresh water suitable for feeding boilers or for return to the stockpile to make more brine.

Over time, soluble impurities build up in the evaporators, and eventually would contaminate the salt crystals. To prevent this, once certain levels are reached the brine is purged and, in addition, the outgoing crystals are washed in clean incoming brine.

Salt crystals which collect in the conical base of the evaporator are removed as slurry and are dried by centrifuge and a fluid bed drier. As a protection against the effects of high humidity, the salt is given a thin coating of anti-caking agent before being passed through the fluid bed drier. The salt from this drier is pure dried vacuum salt (PDV salt) which appears as small, cubic, white crystals.

FURTHER PROCESSING

The salt is produced to various grades of purity, including a range of coarse grades, a range of PDV grades (primarily for food) and BP grades for pharmaceuticals. Coarse crystallised solar salt is made into salt licks for farm animals in salt deficient areas by the addition of other trace minerals and compression into 20 kg blocks by compacting with 20 000 kPa pressure. Table salt is iodised, and has a free-flowing agent added before packaging. PDV salt is sorted into different grain sizes, and the finest grains (which are as fine as flour) are used for baking. Other additives and purity and size gradings are used for the various applications listed above, either by Dominion Salt or by subsidiary companies.

THE ROLE OF THE LABORATORY

The laboratory performs two primary functions: quality control and research. For all grades of salt, routine chemical analysis is performed to ensure purity, and other quality-control tests check the dryness and particle size of the salt.

At Lake Grassmere, work is continuing on finding new ways of increasing production and reducing reliance on the weather, as New Zealand is far from ideal for solar salt production, being situated 42° below the equator. For instance, deep-storage ponds have been extended and new harvesting methods are continually being evaluated. Future problems will be solved by careful investigation and experiment. There is still pioneering to be done because the answers can seldom be found in text-books; surprisingly enough, comparatively little has been written about salt throughout the many centuries that it has been made and prized by man.

ENVIRONMENTAL IMPLICATIONS

The waste materials of salt production have no adverse effects on the environment, as the only wastes produced are bitterns and salt sludges. These come from the sea and can safely be returned to the sea, although the salt sludges are sometimes used in fertiliser instead. In addition, the energy used in the solar salt process is solar and wind energy, and the vacuum process generates its own energy, as well as sometimes producing an excess that can be put onto the national grid.

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J.E. Fergusson; *Inorganic Chemistry and the Earth*; Pergamon Press; 1982

Department of Chemistry, University of Auckland; *Stage One Inorganic Chemistry Laboratory Manual*; Department of Chemistry, University of Auckland; 1995